

Commentary on “Mechanical properties of mono-domain side chain nematic elastomers” by P. Martinoty et al.

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Abstract. We discuss the rheology experiments on nematic elastomers by Martinoty *et al.* in the light of theoretical models for the long-wavelength low-frequency dynamics of these materials. We review these theories and discuss how they can be modified to provide a phenomenological description of the non-hydrodynamic frequency regime probed in the experiments. Moreover, we review the concepts of soft and semi-soft elasticity and comment on their implications for the experiments.

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Nematic elastomers are crosslinked rubbers with the uniaxial symmetry of a nematic liquid crystal [1]. One could argue, therefore, that they are simply uniaxial rubbers. A nematic elastomer can, however, be distinguished from a simple uniaxial elastic medium by the fact that, at least in an idealized limit, it can form via a spontaneous phase transition from an isotropic phase. Since this phase transition breaks the continuous rotational symmetry of the isotropic phase, it has an associated Goldstone mode whose manifestation is the vanishing of the elastic modulus C_5 measuring the elastic energy of strains in planes containing the anisotropy axis [2,3]. Thus, the ideal nematic elastomer has a “soft” elasticity compared to a traditional uniaxial elastic medium in which C_5 is nonzero. In practice, ideal monodomain nematic elastomers do not form in the absence of some aligning field, which is usually produced by weakly crosslinking a sample in the isotropic phase, stretching to produce a uniaxial configuration, and then crosslinking again [4]. The resultant material is weakly anisotropic in the high-temperature paranematic phase and more anisotropic in the low-temperature nematic phase. Since the low-temperature phase arises from an already aligned phase and does not break rotational symmetry, it does not exhibit ideal soft elasticity. Rather, it exhibits “semi-soft” elasticity in which C_5 is small but nonzero. Thus, for small strains, a semi-soft nematic elastomer is truly a uniaxial solid. At higher strains, however, it exhibits properties, such as a nearly constant stress for increasing strain, characteristic of a soft nematic elastomer [5].

The static elastic properties and phase transitions of both soft and semi-soft nematic elastomers are reasonably well understood [1,2,6,7,8], provided the effects of random stresses [2,9] can be ignored. They can be described either in terms of models involving strain only or in terms of models with coupling between a traditional

Maier-Saupe-de-Gennes nematic symmetric-traceless order parameter Q_{ij} and strain. Considerable progress has also been made toward understanding the dynamics of nematic elastomers [10,11,12] again in the limit in which random stresses and fields can be ignored. As in a standard elastic medium, purely hydrodynamical equations, which describe all modes with frequencies ω smaller than the smallest characteristic inverse decay time τ^{-1} when wavenumber q tends to zero, involve only the displacement field \mathbf{u} and not the nematic director \mathbf{n} , which relaxes to the local stain in a nonhydrodynamic time τ_n . Even though the nematic director is not strictly speaking a hydrodynamic variable in either soft or semi-soft nematic elastomers, it is of some interest to develop phenomenological equations describing both nematic director and elastic displacement. Two distinct derivations [1,11,12] lead to identical sets of coupled director-displacement equations, which we will refer to as the NED (nematic-elastomer dynamic) equations, that reduce to the rigorous hydrodynamic equations in terms of displacement only at frequencies $\omega\tau_n \ll 1$ and to the standard equations of nematohydrodynamic when elastic rigidity is turned off.

Rheological measurements of the complex modulus [13]

$$G^*(\omega) = G'(\omega) - iG''(\omega) \quad (1)$$

provide a useful experimental probe of the dynamical properties of viscoelastic systems. They typically probe a wide range of frequencies that stretch from the low-frequency hydrodynamic regime to well above it. Thus, interpreting these experiments requires theoretical models of dynamics beyond hydrodynamics. A nematic elastomer is characterized in general by relaxation times associated with director relaxation and with other modes, which we will simply refer to as elastomer modes. In their simplest form, the NED equations assume the director relaxation time τ_n is the

longest non-hydrodynamic relaxation time, and that it is well separated from the longest elastomer time τ_E . They describe dynamics for both $\omega\tau_n \ll 1$ and $\omega\tau_n > 1$ and provide non-trivial predictions about $G^*(\omega)$, in particular the appearance of a plateau in $G'(\omega)$ and an associated dip in $G''(\omega)$ for $\tau_n^{-1} < \omega < \tau_E^{-1}$. Experiments [14, 15, 16, 17, 18] to date do not exhibit the plateau predicted by the NED equations. This has led Martinoty *et al.* to question their validity.

Here we will review both the hydrodynamical and NED equations for nematic elastomers and discuss how they can be modified to provide a phenomenological description of the non-hydrodynamic frequency regime probed in rheology experiments. Moreover, we review the concepts of soft and semi-soft elasticity and comment on their implications for rheology experiments.

We begin with a review of the dynamics of traditional isotropic solids, of which rubber is a particular example. The elastic free energy of an isotropic solid is characterized by a bulk modulus B and a shear modulus μ , and dissipation is characterized by a bulk viscosity ζ and a shear viscosity η , which are both frequency independent at low frequencies. The complex shear modulus in the hydrodynamic limit is simply

$$G^*(\omega) = \mu - i\omega\eta. \quad (2)$$

This form is rigorous in the hydrodynamic limit where $\omega\tau \ll 1$. μ and η can vary widely in magnitude from system to system. Nothing more can be said about the behavior of $G^*(\omega)$ without some more microscopic model of the dynamics of a particular system.

The Rouse model [19] provides a simple description of the dynamics of polymeric melts. The dynamics of even isotropic elastomers and rubbers is far more complex than that of melts, and the Rouse model does not necessarily provide a good physical description of their dynamical modes. Nevertheless, experimental curves for $G^*(\omega)$ in nematic elastomers are very similar to those predicted by the Rouse model, showing in particular a region in which $G'(\omega)$ and $G''(\omega)$ track each other with a ω^α behavior with $\alpha \approx 1/2$. It is thus legitimate to use Rouse-model predictions as fitting curves for nematic elastomers, whether or not it provides a microscopically correct description of their dynamics. This is the point of view we will take here. We parameterize the complex storage modulus in the isotropic phase of nematic elastomers as

$$G^*(\omega) = G_0[1 + a h_R(-i\omega\tau_E)], \quad (3)$$

where $G_0 = n_x kT$, with n_x being the number density of polymer strands between crosslinks, and $a = \sum_{p=1}^N p^{-2}$. $h_R(x) = x f_R(x)$ is a Rouse function with

$$f_R(x) = \frac{\sum_{p=1}^N (p^2 + x)^{-1}}{\sum_{p=1}^N p^{-2}}. \quad (4)$$

In the limit $N \rightarrow \infty$, the summations in Eq. (4) can be evaluated via the Poisson summation formula with the

result

$$h_R(x) = \frac{3}{\pi^2 \sinh(\pi\sqrt{x})} \{ \pi\sqrt{x} \cosh(\pi\sqrt{x}) - \sinh(\pi\sqrt{x}) \}. \quad (5)$$

When $\omega\tau_E \ll 1$, this expression reduces to Eq. (2) with $\mu = n_x kT$, and $\eta = (\pi^2/6)\mu\tau_E$. When $\tau_E^{-1} < \omega < \tau_n^{-1}$, $G'(\omega) \sim G''(\omega) \sim \sqrt{\omega}$.

A uniaxial solid is characterized by an elastic energy

$$\mathcal{H}_u^R = \int d^3x \left\{ \frac{C_1}{2} u_{zz}^2 + C_2 u_{zz} u_{ii} + \frac{C_3}{2} u_{ii}^2 + C_4 u_{ab}^2 + C_5^R u_{az}^2 \right\}. \quad (6)$$

with five elastic constants, where u_{ij} with $i, j = x, y, z$ is the strain tensor and $a, b = x, y$. The superscript R on the elastic modulus C_5^R for shears in plane containing the z -axis indicates that it has been renormalized by director fluctuations. In soft nematic elastomers, C_5^R is zero, and it is necessary to add bending terms proportional to $(\partial^2 u_a)^2$ to ensure stability in all directions. In practice all single domain nematic elastomers are semi-soft with $C_5^R > 0$, and the bending terms can be neglected. Associated with each of the five elastic constants is a viscosity η_k . The complex storage moduli for shears in the planes containing the z -axis and in the plane perpendicular to the z -axis are, respectively,

$$G_{\parallel}^*(\omega) = C_5^R - i\omega\eta_5^R, \quad (7)$$

$$G_{\perp}^*(\omega) = C_4 - i\omega\eta_4. \quad (8)$$

As in isotropic rubbers, we can say nothing more about the behavior of $G_{\parallel}^*(\omega)$ and $G_{\perp}^*(\omega)$ without some microscopic model of the dynamics. Since there are surely elastomer modes in the anisotropic phase of nematic elastomers, one could argue that they are dominant and that G_{\parallel}^* and G_{\perp}^* have exactly the same form as G in an isotropic system, Eq. (3), with possibly different values of G_0 , a and τ_E . Indeed, the data presented in Martinoty, *et al.* appear to fit this model with $\tau_E \sim 10^{-2}$, considerably longer than the Rouse time in traditional isotropic rubbers. Certainly, however, there are extra director modes in nematic elastomers that are not present in isotropic ones, and a complete model of dynamics beyond hydrodynamics must include them.

A phenomenological approach to the dynamics of nematic elastomers including the nematic director begins with an elastic free energy that includes both strain and the director. Following de Gennes [20], the energy \mathcal{H} can be written as a sum of the Frank free energy \mathcal{H}_n for the director, the strain and strain-director coupling energy

$$\mathcal{H}_{u,n} = \int d^3x \left\{ \frac{C_1}{2} u_{zz}^2 + C_2 u_{zz} u_{ii} + \frac{C_3}{2} u_{ii}^2 + C_4 u_{ab}^2 + C_5 u_{az}^2 + \frac{D_1}{2} Q_a^2 + D_2 u_{za} Q_a \right\}, \quad (9)$$

where

$$Q_a = \delta n_a - \frac{1}{2} (\partial_z u_a - \partial_a u_z). \quad (10)$$

When Q_a relaxes to its equilibrium value $-(D_2/D_1)u_{az}$ in the presence of strain u_{az} , the energy $\mathcal{H}_{\mathbf{u},\mathbf{n}}$ reduces to $\mathcal{H}_{\mathbf{u}}^R$ with $C_5^R = C_5 - D_2^2/(2D_1)$.

The phenomenological equations for \mathbf{n} and \mathbf{u} , which can be derived using standard Poisson-bracket approaches [21], are [12]

$$\dot{n}_i = \lambda_{ijk} \partial_j \dot{u}_k - \Gamma \frac{\delta \mathcal{H}}{\delta n_i}, \quad (11a)$$

$$\rho \ddot{u}_i = \lambda_{kji} \partial_j \frac{\delta \mathcal{H}}{\delta n_k} - \frac{\delta \mathcal{H}}{\delta u_i} + \nu_{ijkl} \partial_j \partial_l \dot{u}_k, \quad (11b)$$

where ν_{ijkl} is an unrenormalized uniaxial viscosity tensor with five independent components, Γ is a dissipative coefficient with dimensions of an inverse viscosity, and

$$\lambda_{ijk} = \frac{\lambda}{2} (\delta_{ij}^T n_k + \delta_{ik}^T n_j) + \frac{1}{2} (\delta_{ij}^T n_k - \delta_{ik}^T n_j), \quad (12)$$

where $\delta_{ij}^T = \delta_{ij} - n_i n_j$. The complex modulus $G_{||}^*(\omega) = C_5^R(\omega)$ predicted by these equations is

$$G_{||}^*(\omega) = C_5 - i\omega \left(\nu_5 + \frac{\lambda^2}{2\Gamma} \right) - \frac{D_2^2}{2D_1} \frac{(1 - i\omega\tau_2)^2}{1 - i\omega\tau_1}, \quad (13)$$

where $\tau_1 = 1/(\Gamma D_1)$ and $\tau_2 = -\lambda/(\Gamma D_2)$. This result is equivalent to the one obtained by Terentjev, Warner and coworkers [1,11]. Equation (13) is a valid expression for the complex modulus provided $\tau_1 \equiv \tau_n$ is much longer than any other nonhydrodynamic relaxation time, including elastomer times, of the system. As can be seen in Fig. 1(a), it predicts a plateau in $G'(\omega)$ for $\omega > \tau_n^{-1}$.

In standard polymeric systems, the Rouse time, τ_R , is of order 10^{-5} s, and light scattering measurements on nematic elastomers yield $\tau_n \sim 10^{-2}$ [22]. It could, therefore, be argued that $\tau_E \sim \tau_R$ and that that $\tau_n \gg \tau_E$. However, liquid crystalline polymers are more viscous than standard polymers, and it is not unreasonable for τ_E to be considerably less than 10^{-5} s. If τ_n and τ_E are of the same magnitude, or if $\tau_n < \tau_E$, then the viscosities and decay times τ_1 and τ_2 in Eq. (13) must be treated as having a frequency dependence when $\omega\tau_E$ is of order 1 or greater.

Since high-frequency dynamics of the nematic phase are expected to be similar to that of the nearly isotropic paranematic phase, ν_5 should have the same behavior as the viscosity in the latter phase:

$$\nu_5(\omega) = \nu_5 f_R(-i\omega\tau_E). \quad (14)$$

In addition, the elastomer modes will affect the relaxation of director modes. Indeed, the light scattering experiments of Ref. [22] indicate a very broad distribution of director relaxation times. There is no reason why many closely spaced modes should not lead to a behavior of Γ^{-1} with a Rouse-like form,

$$\Gamma(\omega)^{-1} = \Gamma^{-1} f_R(-i\omega\tau_E). \quad (15)$$

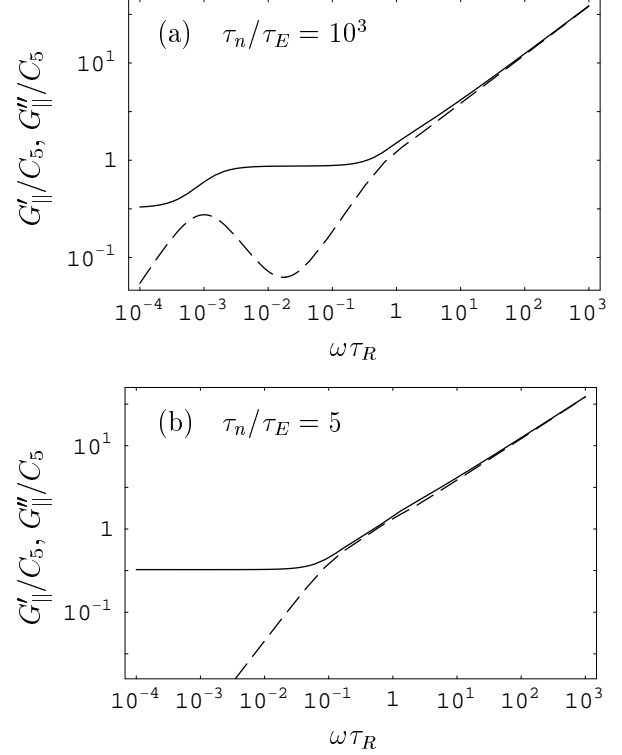


Fig. 1. Log-log plot of the reduced storage and loss moduli $G'_{||}/C_5$ (solid lines) and $G''_{||}/C_5$ (dashed lines) versus the reduced frequency $\omega\tau_E$ as given respectively by the real and imaginary parts of Eq. (16) (a) for $\tau_n/\tau_E = 10^3$ and (b) for $\tau_n/\tau_E = 5$. For the purpose of illustration we have set, by and large arbitrarily, $\nu_5/(C_5\tau_E) = 1.8$, $D_1/C_5 = 0.0135$, $D_2/D_1 = 10$ and $\lambda = -1$.

With this assumption, a reasonable phenomenological form for the complex modulus $G_{||}^*(\omega)$ that incorporates the effects of both Rouse and director modes is

$$G_{||}^*(\omega) = C_5 + \left(\frac{\nu_5}{\tau_E} + \frac{\lambda^2}{2} \frac{\tau_n}{\tau_E} D_1 \right) h_R(-i\omega\tau_E) - \frac{D_1}{2} \left(\frac{D_2}{D_1} \right)^2 \frac{[1 - \lambda(D_1/D_2)(\tau_n/\tau_E) h_R(-i\omega\tau_E)]^2}{1 + (\tau_n/\tau_E) h_R(-i\omega\tau_E)}. \quad (16)$$

$G_{\perp}^*(\omega)$, on the other hand, has the same form as for an isotropic system, cf. Eq. (3). The storage and loss moduli $G'_{||}(\omega)$ and $G''_{||}(\omega)$ implied in Eq. (16) are plotted in Fig. 1. If $\tau_n \leq \tau_E$ the frequency dependence of the moduli is dominated by the elastomer modes with $G'_{||}(\omega) = C_5^R$ and $G''_{||}(\omega) = \nu_5^R \omega$ with $\nu_5^R = \nu_5 + [\lambda^2/(2\Gamma)](1 - \tau_1/\tau_2)^2$ for $\omega\tau_E \ll 1$ and $G'_{||}(\omega) \sim G''_{||}(\omega) \sim \sqrt{\omega}$ for $\omega\tau_E \gg 1$. If $\tau_n \gg \tau_E$, however, the structure is much richer. In addition to the behavior for $\tau_n \leq \tau_E$, the storage and loss moduli develop respectively a noticeable plateau and dip at intermediate frequencies.

Two experimental groups, the Cambridge group [14, 16,17] and the Martinoty group [15,18], have reported ex-

tensive measurements of G_{\parallel}^* and G_{\perp}^* on a variety of samples. The paper of Martinoty group shows curves of $G'_{\parallel}(\omega)$ and $G''_{\parallel}(\omega)$ that are very similar to those in Fig. 1(b) for $\tau_n/\tau_E = 5$. Remarkably, the experimental curves are also compatible Fig. 1(a) where $\tau_n/\tau_E \ll 1$ if one ignores the low-frequency part of the theoretical curves.

In their simplest form in which Γ is independent of frequency, the NED equations treat the non-hydrodynamic director modes but no other non-hydrodynamic modes. Ignoring other non-hydrodynamic modes is only justified if there is a clear separation of time scales with $\tau_1 \gg \tau_E$. Martinoty *et al.* argue convincingly that their data is incompatible with this assumption. Indeed the Cambridge group does not disagree with this observation at least in some materials since in Ref. [17], they indicate explicitly that there is insufficient separation of time (actually frequency) scales for the intermediate plateau shown in Fig. 1(a) to be observed. Our view is that the experimental evidence is that τ_n is of order τ_E in current experimental systems, though current data does not rule out the possibility of τ_n being as much as 5 times greater than τ_E as a comparison of Fig. 1(b) and the Martinoty data shows. Though it seems unlikely that $\tau_n \gg \tau_E$, one cannot even rule out this possibility entirely on the basis of the current experimental data, because the frequencies in the experiments might not be low enough to probe τ_n^{-1} if τ_n is greater than several hundred seconds. As a comparison of the experimental curves and Fig. 1(a) shows, there is a danger of overlooking the intermediate plateau in G'_{\parallel} and the dip in G''_{\parallel} if frequencies less than τ_n^{-1} are not probed.

The measurements by the Cambridge group and the Martinoty group include 2 samples each prepared in the same way by both groups. For these samples, the curves for G'_{\perp} as a function of temperature T at different ω are very similar. At each frequency, G'_{\perp} shows a general upward trend with decreasing T as the glass transition is approached. At the lowest frequency, there is a measurable dip in the vicinity of the IN transition, though that reported by the Martinoty group is smaller than that reported by the Cambridge group. The magnitude of this dip decreases with increasing frequency. Both groups also report a decrease in $G'_{\parallel}/G'_{\perp}$ at the IN transition.

To an impartial reader, the data obtained by the two groups are qualitatively if not quantitatively similar. The two groups, however, provide different interpretations of their data. The Cambridge group interprets the dip in $G'_{\parallel}/G'_{\perp}$ as a manifestation of dynamic softening associated with the transition from uniaxial paranematic phase to the semi-soft nematic phase whereas the Martinoty group says that the dip is simply explained in terms of the de Gennes model, in which the reduction of G_{\parallel} arises from the D_2^2/D_1 term, without recourse to the concept of semi-soft elasticity.

The de Gennes theory for nematic elastomers defined by the total elastic energy \mathcal{H} provides a correct description of any uniaxial elastomer regardless of how it is formed. A soft uniaxial elastomer formed via spontaneous symmetry breaking from an isotropic elastomer is merely one with

$C_5^R = C_5 - D_2^2/(2D_1) = 0$. Since the high-temperature phase of single-domain nematic elastomers are at least weakly uniaxial, it is true that all single-domain phases can be described by the de Gennes model without invoking the concepts of soft or semi-soft elasticity. This approach, however, misses the fact that the vanishing of C_5^R and the resultant soft elasticity in nematic phases formed spontaneously from isotropic elastomers is a consequence of symmetry and not of arbitrary juggling of parameters. A transition from a weakly uniaxial paranematic phase to a more strongly uniaxial nematic phase will be accompanied by a decrease in C_5^R that increases as the anisotropy of the paranematic phase decreases. In the resultant semi-soft nematic phase, C_5^R vanishes with the anisotropy of the paranematic phase. Our preference is to use the concepts of soft and semi-soft elasticity to describe the reduction of C_5^R that arise from the paranematic-to-nematic transition. We agree, however, that these concepts become less meaningful in samples that are really above the mechanical critical point [23] at which this transition becomes continuous. Being above this critical point is, however, incompatible with the large plateau in the semi-soft nonlinear stress strain curve [24]. The Martinoty data does seem to be consistent with being above the mechanical critical point. If it is, then we would like to see experiments done on materials that are softer in the nematic phase if they really do exist.

The dynamics of nematic elastomers are clearly very complicated. They have all of the complexity of rubbers and gels, which have localized gel and other modes that we have not even discussed and eventual transitions to glassy phases, in addition to that of nematics. In spite of these complexities, the experimental results for the complex storage modulus of a number of samples of nematic elastomers measured by two groups are remarkably similar. Neither group finds a truly soft nematic phase with a shear modulus an order of magnitude or more smaller than it is in the high-temperature nearly isotropic phase, but their data can be described in the context of semi-soft elasticity.

The above discussion summarizes what current theories can say about the equilibrium rheological properties of homogeneous nematic elastomers. The only rigorous statement is that semi-soft nematic elastomers are uniaxial solids with frequency-independent shear moduli and viscosities in the low-frequency limit. At higher frequencies, contributions from non-hydrodynamic modes, including director relaxation, contribute to the complex moduli. Though experiments seem to be converging to reproducible results, it is clear that there is much more to do before we have a complete understanding of the dynamics of nematic elastomers.

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